

Supplementary Information

Evidence for defect-mediated tunneling in hexagonal boron nitride-based junctions

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1. Characterization of hexagonal boron nitride (hBN) flakes

The hBN flakes were mechanically exfoliated on to SiO₂/Si wafers with either 285nm or 300nm oxide. We then employed a combination of optical microscopy, atomic force microscopy and Raman spectroscopy to identify the uniformity and number of layers in the exfoliated flakes. In the present study we have used three different batches of hBN crystals and no significant differences between the different crystals were observed.

1.1 Optical microscopy

A BH2-UMA Olympus microscope with a Nomarski interference contrast (NIC) prism attachment was used to identify thin-layers of hBN. The NIC attachment helps in identifying regions of uniform thickness in the hBN flake, which are harder to distinguish otherwise. For instance, Fig S1 shows hBN regions of varying thicknesses. The contrast is much better with the NIC attachment.

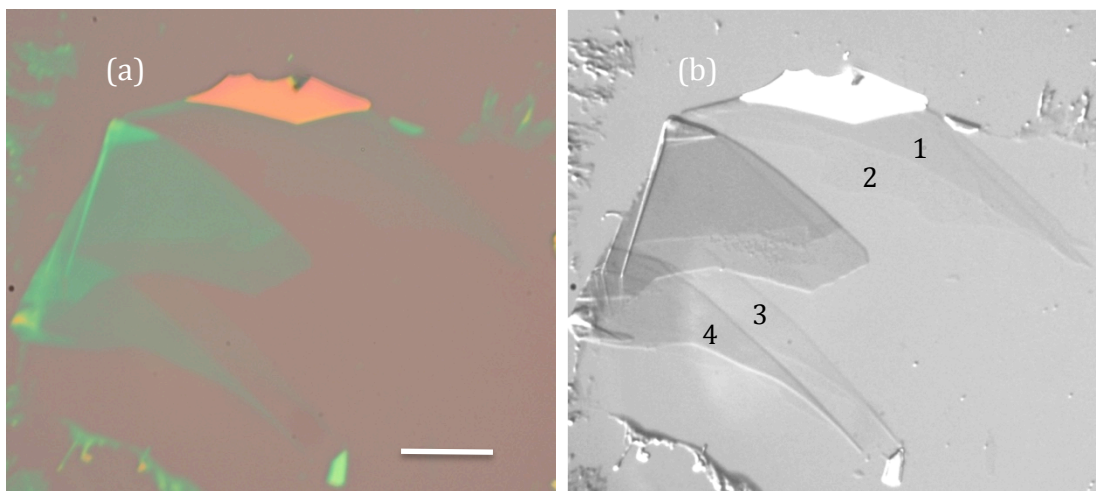


FIG S1. Optical micrographs (a) without and (b) with the NIC attachment (in grayscale) showing the enhanced contrast between regions of different thicknesses. In (b), some of the uniform regions are marked as 1-4. Scale bar is 20 μ m.

1.2 Atomic Force Microscopy

Atomic force microscopy (AFM) was used as one of the tools to determine the number of hBN atomic layers. We have used Multimode-8 AFM with a Nanoscope V controller. For the

tunneling devices, flakes with uniform thickness were identified. Figure S2(a) shows a representative AFM topographic image of two hBN flakes. Line cuts taken at three regions marked as blue, red and green show clear steps at the flake boundaries. The thickness is estimated to be about 0.65nm indicating that the flakes consist of two atomic layers.

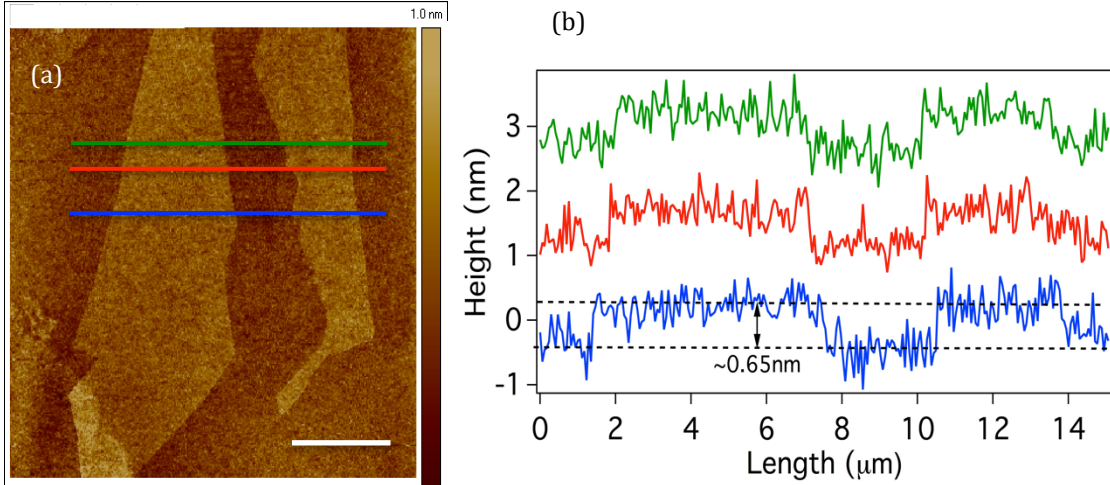


Fig. S2. (a) AFM topographic image of two hBN flakes on a SiO₂/Si wafer. Scale bar is 5μm. (b) Height profiles corresponding to the blue, red and green lines shown in (a). The thickness is estimated to be ~0.65nm.

We often find flakes with multiple layers. AFM helps in identifying regions of uniform thickness. Figure S3 shows an AFM image with line profiles at two locations for a predominantly 4 atomic layered flake (~1.3nm), with a 3 atomic layered edge (~0.9nm).

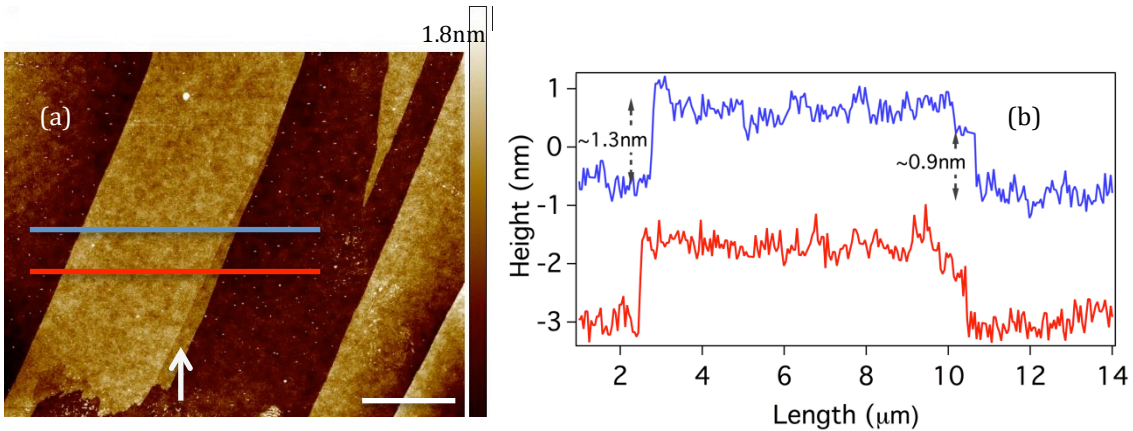


Fig.S3: (a) AFM topography image and two line profiles marked in red and blue for an hBN flake with 4 atomic layers, containing a 3 layered edge shown by the pointed arrow. The line profile captures the two different layer thicknesses. The scale bar is 5μm.

1.3 Raman Spectroscopy

We have used a Renishaw M1000 micro Raman spectrometer system with a solid state 100mW, 514.3 nm green laser light to identify the number of layers. Hexagonal boron nitride gives a Raman peak around 1366 cm^{-1} [1]. While the peak position didn't show a clear variation with the number of layers, the Raman intensity was found to increase with the number of layers as shown in Fig. S4(a) [1]. The integrated intensity is plotted as a function of the number of layers in Fig. S4(b). Since the Raman intensity and the base line can change slightly over time or based on how you set the system up, we use an eight-layered boron nitride flake as a calibration point for every run and verify the integrated intensity of this particular calibration device with the value marked with an arrow in Fig. S4(b). The integrated intensity of the hBN flakes determined using this protocol gives a reasonable estimate of the layer thickness and matches very well with the estimates given by the AFM line profiles.

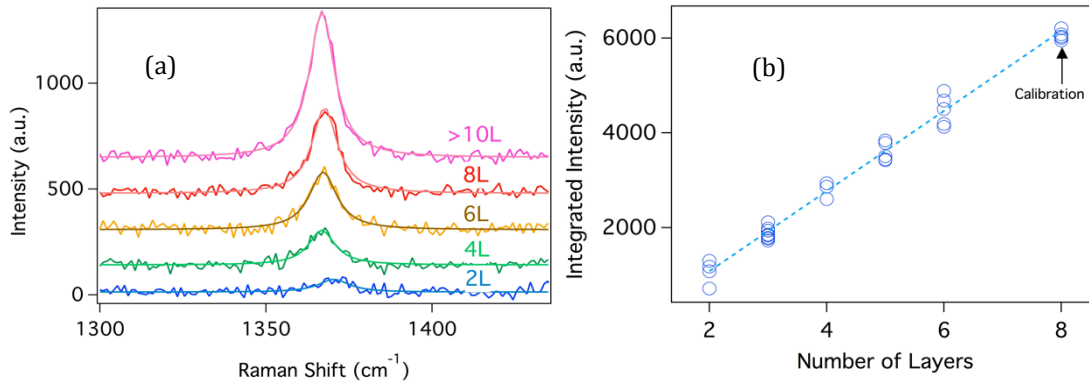


Fig. S4 (a) Raman spectra for hBN flakes with 2-10 atomic layers. The lines are Lorentzian fits. (b) Integrated intensity vs. number of monolayers of hBN, showing a steady increase with thickness. The calibration point is marked with an arrow.

Raman spectra acquired over different regions on hBN flakes with multiple layers is a good indicator of the uniformity of the flakes as well. Figure S5 shows an optical image of an hBN flake with regions of two different thicknesses marked A and B. Raman spectra taken at various points on the two different regions clearly show that the regions are uniform and distinct in thickness. Region A and B were estimated to be 3 and 5 atomic layers respectively.

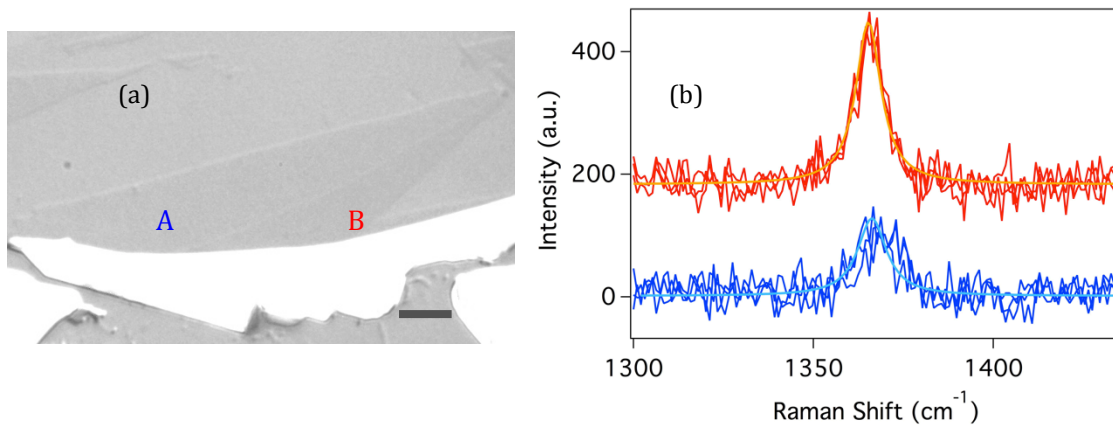


Fig S5: (a) A grayscale optical micrograph of an hBN flake, taken with the NIC attachment showing two regions with different layer numbers marked as A and B. Scale bar is 10 μ m. (b) Raman spectra taken at three locations each in regions A (blue) and B (red) show a difference in intensity across the two regions and uniformity within each region. The lines are Lorentzian fits.

2. Fabrication of hBN-based tunnel junctions

2.1. Cr/Au-hBN-Cr/Au devices

Bottom electrodes: For the Cr/Au based tunnel junctions, electron beam lithography was used to pattern many parallel bottom electrodes on a highly p-doped Si wafer with a 285nm oxide layer. The Cr/Au pads were thermally evaporated. We have experimented with two different thicknesses for the bottom electrodes: 5/15nm and 5/120nm of Cr/Au respectively. While the transport characteristics showed no visible differences, we found that the hBN flake adhered better to the 5/15nm electrodes and gave a higher yield, possibly due to the lower height difference between the electrodes and the atomically thin hBN layer.

Pick up and transfer of hBN flake: We have used the pick-up technique by Wang et. al. [2] to pick the thin hBN layer and transfer to the bottom electrodes. A polymer stamp made of polydimethylsiloxane (PDMS) and 4% polypropylene carbonate (PPC) in chloroform was affixed on a glass slide with the PPC layer facing up. This stamp was attached to an XYZ micromanipulator stage. The Si/SiO₂ wafer with the exfoliated hBN was placed on a heated optical microscope stage (at about 50°C). The PDMS/PPC stack was aligned on this hBN flake, left for about 5 minutes and allowed to cool slightly before lifting the stack up. The hBN adheres to the PDMS/PPC stack and gets picked up. The hBN flake is then made to align with the pre-patterned bottom electrodes on the Si/SiO₂ wafer. The stack is lowered to make contact with the electrodes and heated to about 90-100°C. The glass slide and the PDMS can now be removed, while the PPC layer stays on the wafer, which can be removed with chloroform.

Top electrode: The top electrode consisted of a single lithographically defined 5/120nm Cr/Au pad, which formed multiple tunnel junctions with the many parallel bottom

electrodes underneath the hBN flake. Thus each device consisted of many Cr/Au-hBN-Cr/Au tunnel junctions.

2.2. Graphite-hBN-Graphite devices

We have fabricated two different kinds of graphite-based junctions, which are detailed below.

2.2.1 Step-by-step transfer of individual layers

Bottom electrode: The graphite layers were mechanically exfoliated from Kish graphite on a SiO₂/Si wafer and patterned using electron beam lithography and oxygen plasma etching, thus forming multiple bottom electrodes.

Pick-up and transfer of hBN: The same protocol as described in section 2.1 was followed to pick up and transfer the hBN flakes. The flakes were found to adhere well to the graphite electrodes, which had large atomically smooth surfaces.

Top electrode: The top layer graphite was peeled directly on a PDMS/PPC stack and transferred on the graphite/hBN stack as described above. The top graphite was then lithographically patterned and oxygen plasma etched to form multiple tunnel junctions.

2.2.2. Dry transfer to form graphite-hBN-graphite stacks

We also fabricated graphite-hBN-graphite junctions as a single stack. This provided clean interfaces as the individual layers never came in contact with polymer residues from the fabrication procedure. In this method, a thin and long graphite flake was identified on a SiO₂/Si wafer, which formed the bottom electrode. The top graphite electrode was directly exfoliated on a PDMS/PPC stack and aligned with the hBN as described above. The hBN adheres well to the graphite and is picked up. The graphite/hBN stack is deposited on the bottom electrode, to form a single tunnel junction. Electron beam lithography was subsequently done to define the external electrical leads.

References:

1. Gorbachev, R. V.; Riaz, I.; Nair, R. R.; Jalil, R.; Britnell, L.; Belle, B. D.; Hill, E. W.; Novoselov, K. S.; Watanabe, K.; Taniguchi, T.; Geim, A. K.; Blake, P. *Small* **2011**, 7 465-468.
2. Wang, L.; Meric, I.; Huang, P. Y.; Gao, Q.; Gao, Y.; Tran, H.; Taniguchi, T.; Watanabe, K.; Campos, L. M.; Muller, D. A.; Guo, J.; Kim, P.; Hone, J.; Shepard, K. L.; Dean C. R. *Science* **2013**, 342, 614-617.